



PATENT SPECIFICATION

NO DRAWINGS

870.027

Date of Application and filing Complete Specification: Aug. 19, 1959.

No. 28372/59.

Application made in United States of America on Sept. 30, 1958.

Complete Specification Published: June 7, 1961.

Index at acceptance:—Classes 2(3), C1F3(B: D3), C2A(3: 5: 9: 13: 14), C2B(5: 27), C2R(18: 20), C2(S15: T15); and 98(2), D7.

International Classification:—C07d. G03c.

COMPLETE SPECIFICATION

Aminopyridinediazonium Salts

We, GENERAL ANILINE & FILM CORPORATION (Assignees of RALPH GOWER DAVIES MOORE and ROBERT JAMES COX), a corporation of the State of Delaware, United States of America, located at 230 Park Avenue, New York 17, State of New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to aminopyridinediazonium salts and, especially to the use of said salts in the diazotype process.

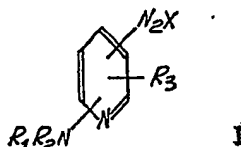
The diazotype process, as is known, involves sensitization of a base such as paper with a light-sensitive diazo compound, exposing the sensitized material under a pattern to burn out the diazo where the light strikes and developing an image by coupling the undecomposed diazo with an azo dye coupling component in the presence of a base such as ammonia or sodium hydroxide. The speed and over-all utility of this process depend upon the rapidity and degree that the diazonium compound is burned out on exposure, the rapidity with which the diazo couples to form azo dye and the density of dye image obtained.

Many diazonium compounds have been recommended for use in manufacturing diazotype materials. For the most part, these diazos are derived from *p*-phenylenediamines. While these compounds produce satisfactory materials for the diazotype process, they still leave much to be desired from the standpoint of the speed of the material, the density of the images and the rate of development.

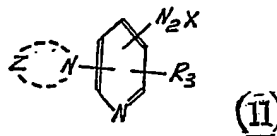
We have now found that diazonium compounds which meet the prerequisites of the diazotype art to a very high degree are aminopyridinediazonium salts in which the amino group is secondary or tertiary. Such diazonium compounds and their use in light-sensitive diazotype materials constitute the subject of the present invention.

According to the present invention there is

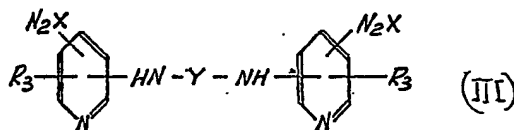
provided an aminopyridinediazonium salt having the general formula:



or the general formula



or the general formula



in which R_1 is hydrogen, alkyl e.g. methyl, ethyl, propyl, butyl, aryl of the benzene series e.g. phenyl, tolyl, diethylaminophenyl, dimethylaminophenyl, pyridyl or aralkyl e.g. benzyl and R_2 may be alkyl as above, aryl as above, pyridyl, or aralkyl as above; Z represents the atoms necessary to complete a 6-membered hydrogenated heterocyclic ring system; R_3 is hydrogen or alkyl as above; X is an anion e.g. halide, sulfate, nitrate; and Y is diphenyl or benzylphenyl.

Examples of the compounds of this invention which we have found to be eminently suitable are:

6 - dimethylamino - 3 - pyridinediazonium chloride and its zinc chloride, stannic

- chloride, cadmium chloride, mercuric chloride, boron trifluoride double salts
- 6 - diethylamino - 3 - pyridinediazonium chloride and its aforementioned double salts
- 5 6 - methylamino - 3 - pyridinediazonium chloride and its aforementioned double salts
- 6 - ethylamino - 3 - pyridinediazonium chloride and its aforementioned double salts
- 6 - morpholino - 3 - pyridinediazonium chloride
- 10 6 - piperazino - 3 - -pyridinediazonium chloride
- 6 - benzylamino - 3 - pyridinediazonium chloride
- 15 6 - *p* - toluidino - 3 - pyridinediazonium chloride
- 6 - (*p* - dimethylaminoanilino) - 3 - pyridine-diazonium chloride
- N_2N^+ - (4,4' - biphenylene)bis(6 - amino - 3-pyridinediazonium chloride)
- 6 - anilino - 3 - pyridinediazonium chloride
- 6 - (2 - pyridylamino) - 3 - pyridinediazonium chloride
- 6,6' - (*p,p'* - methylenedianilino)bis(3 - pyridinediazonium chloride)
- 25 N - methyl - 6 - anilino - 3 - pyridinediazonium chloride
- 6 - diethylamino - 5 - methyl - 3 - pyridine-diazonium chloride
- 2 - dimethylamino - 3 - pyridinediazonium chloride
- 30 The couplers with which the diazonium salts were used are those normally employed in diazotype materials. Below is a list of couplers which can be used with our diazonium compounds and the color produced therewith:
- 35

Coupler	Dye Color
Resorcinol	sepia
6,7-Dihydroxy-2-naphthalene-sulfonic acid	reddish purple
2,3-Naphthalenediol	reddish purple
Acetoacetanilide	yellow
Phloroglucinol	reddish brown
<i>m</i> -Hydroxyphenylurea	sepia
<i>N</i> -benzylacetoacetamide	yellow
3-Methyl-1-phenyl-5-pyrazolone	orange
<i>N</i> - <i>o</i> -methoxyphenyl-3-hydroxy-2-naphthamide	blue-purple
4,4'-Thiodiresorcinol	red to sepia

In preparing our novel compounds, we have found it to be generally more convenient to form the double salt of the compound with an inorganic salt for example, zinc chloride, stannic chloride, cadmium chloride, mercuric chloride, boron trifluoride, and to isolate our novel compounds in the form of such double salts.

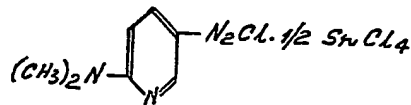
Below he have given a number of examples of our novel compounds and processes for their preparation. It is to be understood, however, that these examples are given by way of illustration only and not by way of limitation.

EXAMPLE I.

6-Dimethylamino-3-pyridinediazonium chloride.

A solution of 1.7 g. of 5 - amino - 2 - dimethylaminopyridine hydrochloride in 10 ml. of hydrochloric acid (sp. gr. 1.19) was cooled with stirring to 0° C. and treated dropwise

with 5 M sodium nitrite at 0—5° C. until an excess of nitrite remained in the solution. About 2 g. of solid stannic chloride pentahydrate were added, whereupon a yellow solid precipitated which was filtered and dried. It melted at 165° C. with decomposition and was probably a complex salt of the diazo with the following structure:



5 - Amino - 2 - dimethylaminopyridine hydrochloride was isolated in 78% yield by the reduction of 2.19 g. of 2-dimethylamino-5-nitropyridine in 50 ml. of isopropyl alcohol under 3—4 atmospheres of hydrogen over palladium on carbon catalyst. The catalyst was filtered off and anhydrous hydrogen chloride

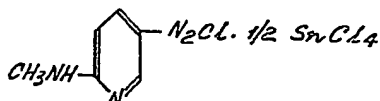
was passed into the solution to precipitate the amine hydrochloride which was recrystallized from an isopropyl alcohol-water mixture. It melted at 260° C. with decomposition.

- 5 2 - Dimethylamino - 5 - nitropyridine, m. 154—5° C., was obtained by nitration of 2-dimethylaminopyridine, b. 81—85° C./15 mm., which was prepared by methylation of 2 - aminopyridine with dimethyl sulfate and
10 sodamide (Ber. 61, 429).

EXAMPLE II.

6-Methylamino-3-pyridinediazonium chloride.

- A solution of 7.6 g. of 5 - amino - 2-methylaminopyridine hydrochloride in 20 ml. of hydrochloric acid (sp. gr. 1.19) cooled to between 0—5° C. with stirring was treated dropwise with 7.8 ml. of 5 M sodium nitrite solution, the temperature being held at 5° C. or lower. 5 G. of stannic chloride pentahydrate were added to the solution and the resultant slurry of dark solid was stirred for 15 minutes. The precipitate was filtered, washed with a brine solution, and dried. It weighed
25 10.2 g., melted at 154° C. with decomposition, and probably had the structure:



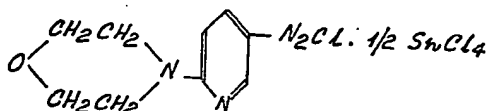
- 5 - Amino - 2 - methylaminopyridine hydrochloride was prepared by the reduction of 8.9 g. of 2 - methylamino - 5 - nitropyridine in 200 ml. of ethanol under 3—4 atmospheres pressure of hydrogen over palladium on carbon catalyst. The catalyst was filtered off and anhydrous hydrogen chloride was passed into the filtrate until a dark precipitate appeared. The precipitate was filtered and washed, first with ethanol, then with ether. It weighed 7.6 g., which corresponds to a yield of 67%, and melted at 239—41° C. with decomposition.
40 2 - Methylamino - 5 - nitropyridine, m. 180—1° C., was prepared in 92% yield by the action of methylamine on 2 - chloro - 5-nitropyridine, m. 106—8° C., which in turn was prepared from 2 - aminopyridine by nitration, diazotization, hydrolysis and finally reaction with phosphorus pentachloride (J. Chem. Soc. 1941, 12).

EXAMPLE III.

6-Morpholino-3-pyridinediazonium chloride.

- A slurry of 10 g. of 5 - amino - 2 - morpholinopyridine hydrochloride in 10 ml. of hydrochloric acid (sp. gr. 1.19) and 15 ml. of water was cooled to 0° C. with stirring. 11.6 ml. of 5 M sodium nitrite were added dropwise, not allowing the temperature to rise above 5° C. 3 g. of stannic chloride pentahydrate were added to the yellow solution and a yellow
50
55

brown solid precipitated. Stirring was continued for one-half hour and after standing in the cold overnight, the precipitate was filtered, washed with a brine solution and dried. It weighed 4.7 g., melted at 162° C. with decomposition, and probably had the structure:



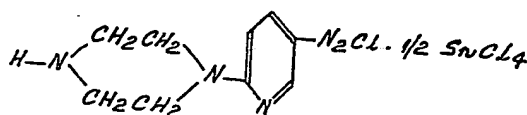
5 - Amino - 2 - morpholinopyridine hydrochloride was prepared in 90% yield by hydrogenating 2 - morpholine - 5 - nitropyridine in ethanol at 3—4 atmospheres pressure over palladium on carbon catalyst. The catalyst was filtered off and anhydrous hydrogen chloride was passed into the filtrate until a white solid precipitated which melted at about 250° C. with decomposition.

2 - Morpholino - 5 - nitropyridine, m. 142—3° C., was prepared in 75% yield by reaction of morpholine with 2 - chloro - 5-nitropyridine prepared as outlined in Example II.

EXAMPLE IV.

6-Piperazino-3-pyridinediazonium chloride.

A solution of 3.1 g. of 5-amino-2-piperazinopyridine hydrochloride in 5 ml. of hydrochloric acid (sp. gr. 1.19) and 5 ml. of water was cooled to 0° C. with stirring and treated with 2 g. of stannic chloride pentahydrate. Then 2.2 ml. of 5 M sodium nitrite were added dropwise, the temperature not being allowed to rise above 5° C. Stirring was continued for 15 minutes and the yellow product was collected by filtration, washed with water and dried. It weighed 1.5 g., melted at 160° C. with decomposition, and probably had the structure:



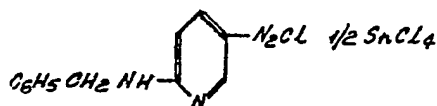
5 - Amino - 2 - piperazinopyridine hydrochloride was made in 76% yield by the reduction of 3.3 g. of 2 - piperazino - 5 - nitropyridine in ethanol at 3—4 atmospheres pressure of hydrogen over palladium on carbon catalyst. The catalyst was filtered off and a white solid was precipitated by passing anhydrous hydrogen chloride through the filtrate. It melted over the range 240—45° C. with decomposition.

2 - Piperazino - 5 - nitropyridine, m. 84—5° C., was prepared in 24% yield by reaction of piperazine with 2 - chloro - 5 - nitropyridine obtained as in Example II.

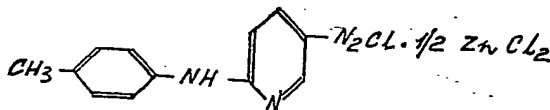
EXAMPLE V.

6-Benzylamino-3-pyridinediazonium chloride.

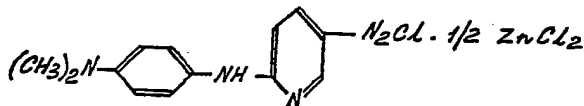
- A solution of 6.5 g. of 5 - amino - 2-benzylaminopyridine hydrochloride in 2.2 ml. of hydrochloric acid (sp. gr. 1.19) and 100 ml. of water was cooled to 0° C. with stirring and was treated with 6 ml. of 5 M sodium nitrite. The solution was allowed to stir for one-half hour and then 10.5 g. of stannic chloride pentahydrate were added and the yellow solid that precipitated was collected by filtration and dried. It weighed 6.4 g., melted at 155° C. with decomposition, and probably had the structure:



- 5 - Amino - 2 - benzylaminopyridine hydrochloride was prepared in 89% yield by the reduction of 7.4 g. of 2 - benzylamino - 5 - nitropyridine in 250 ml of isopropyl alcohol at 3—4 atmospheres of hydrogen pressure



- 5 - Amino - 2 - p - toluidinopyridine hydrochloride was prepared in 82% yield by reduction of 2 - p - toluidino - 5 - nitropyridine in ethanol at 3—4 atmospheres pressure of hydrogen over palladium on carbon catalyst. The catalyst was filtered off and anhydrous hydrogen chloride was passed into the filtrate until a white solid precipitated. It melted over the range 237—42° C. with decomposition.
- 2 - p - Toluidino - 5 - nitropyridine, m. 136—70° C., was prepared in 68% yield by condensation of p - toluidine with 2 - chloro - 5 - nitropyridine (Example II).



- 5 - Amino - 2 - (p - dimethylaminoanilino) - pyridine hydrochloride was prepared by the reduction of 2 - (p - dimethylamino anilino) - 5 - nitropyridine in ethanol at 3—4 atmospheres pressure of hydrogen over palladium on carbon catalyst. The catalyst was filtered off and anhydrous hydrogen chloride was passed into the solution until a white solid precipitated. The yield of hydrochloride was 90% of theory and it melted at 245° C. with decomposition.
- 2 - (p - Dimethylaminoanilino) - 5 - nitro-

over palladium on carbon catalyst. The catalyst was filtered off and anhydrous hydrogen chloride was passed into the filtrate. A white solid was precipitated by the addition of about one liter of ether. It melted over the range 210—20° C. with decomposition.

2 - Benzylamino - 5 - nitropyridine, m. 131—4° C., was prepared in 51% yield by the condensation of benzylamine with 2-chloro - 5 - nitropyridine prepared as in Example II.

EXAMPLE VI.

6-p-Toluidino-3-pyridinediazonium chloride.

A solution of 8.3 g. of 5 - amino - 2 - p - toluidinopyridine hydrochloride in 25 ml. of hydrochloric acid (sp. gr. 1.19) and 75 ml. of water was cooled to 0° C. with stirring. 7 ml. of 5 M sodium nitrite was added dropwise, the temperature not being allowed to rise above 3° C. To this solution were added 30 ml. of 60% zinc chloride solution and the stirring was continued for one-half hour. The yellow solid which precipitated was filtered and dried. It weighed 10.8 g., melted at 137° C. with decomposition, and probably had the structure:

EXAMPLE VII.

6-(p-Dimethylaminoanilino)-3-pyridinediazonium chloride.

A solution of 8.5 g. of 5 - amino - 2 - (p - dimethylaminoanilino) - pyridine hydrochloride in 15 ml. of hydrochloric acid (sp. gr. 1.19) and 35 ml. of water was treated slowly with 6.5 ml. of 5 M sodium nitrite. To this solution were added 20 ml. of 60% zinc chloride solution and stirring was continued for one-half hour. The yellow product was filtered and dried. It weighed 9.0 g., melted at 128° C. with recomposition, and probably had the structure:

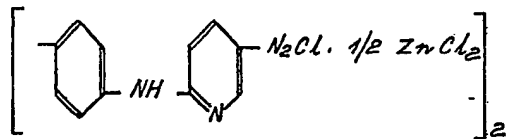
EXAMPLE VIII.

N,N'-(4,4'-Biphenylene)bis(6-amino-3-pyridinediazonium chloride).

2 g. of N,N' - bis(5-nitro-2-pyridyl) benzidine were slurried with 12.5 ml. of hydrochloric acid (sp. gr. 1.19) and 12.5 ml. of water. Zinc powder was added portionwise

with continued stirring until a very pale yellow solution was obtained. The excess zinc was filtered off and ice was added to the filtrate until the temperature had dropped to 5° C.

- 5 This solution was treated dropwise with 5 M sodium nitrite until it showed free nitrite ion. The orange yellow precipitate was filtered and dried. It weighed 0.5 g., melted at 106° C. with decomposition, and probably had the structure:

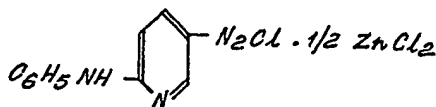


- 15 Crude N,N'-bis(5-nitro-2-pyridyl)-benzidine, which did not melt at 320° C., was prepared in almost quantitative yield by the condensation of benzidine with 2-chloro-5-nitropyridine prepared as in Example II.

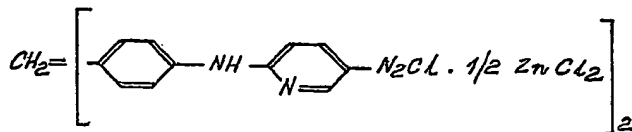
EXAMPLE IX.

6-Anilino-3-pyridinediazonium chloride.

- 20 A solution of 9.1 g. of 5-amino-2-anilinopyridine hydrochloride in 25 ml. of hydrochloric acid (sp. gr. 1.19) and 55 ml. of water was cooled with stirring to 0° C. This solution was treated with 20 ml. of a 60% solution of zinc chloride and then slowly with 25 7.9 g. of 5 M sodium nitrite solution. The reaction mixture was stirred for one-half hour and then allowed to stand in the cold overnight. The yellow precipitate was filtered, washed with a little water, and dried. It 30 weighed 9.9 g., melted with decomposition at 128° C., and probably had the structure:



- 35 5-Amino-2-anilinopyridine hydrochloride was prepared in 76% yield by the hydrogenation of 2-anilino-5-nitropyridine in ethanol at 3-4 atmospheres pressure over palladium on carbon catalyst. The catalyst was filtered off and anhydrous hydrogen chloride was passed into the filtrate until a white solid precipitated, which was filtered, washed with ether, and dried. It melted with 40 decomposition over the range 219-23° C.

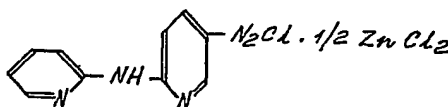


2-Anilino-5-nitropyridine, m. 134-7° C. (Ann. 518, 274-89 (1935)), was prepared in 54% yield by the action of aniline on 2-chloro-5-nitropyridine (Example II).

EXAMPLE X.

6-(2-Pyridylamino)-3-pyridinediazonium chloride.

A slurry of 1.5 g. of 5-amino-2-(2-pyridylamino)-pyridine hydrochloride with 5 ml. of hydrochloric acid (sp. gr. 1.19) and 15 ml. of water was cooled in an ice bath. 1.3 ml. of 5 M sodium nitrite were slowly added with stirring and the resultant yellow solution was treated with a few milliliters of 60% zinc chloride solution. The yellow precipitate was filtered, washed with a little water, and dried. It weighed 2.1 g., melted at 185° C. with decomposition, and probably had the structure:



5-Amino-2-(2-pyridylamino)pyridine hydrochloride was prepared in 98% yield by the reduction of 2-(2-pyridylamino)-5-nitropyridine in isopropyl alcohol under 3-4 atmospheres pressure of hydrogen over palladium on carbon catalyst. The catalyst was filtered off and a few drops of hydrochloric acid (sp. gr. 1.19) were added to the filtrate. The white solid which precipitated was collected.

2-(2-Pyridylamino)-5-nitropyridine was prepared according to Chichibabin and Preobrazhenskii (Ber. 61, 203 (1928)) by the action of 2-aminopyridine on 2-chloro-5-nitropyridine (Example II).

EXAMPLE XI

6,6'-(p,p'-Methylene dianilino)bis(3-pyridinediazonium chloride).

A solution of 1.7 g. of 5,5'-diamino-2,2'-(p,p'-methylenedianilino)dipyridine hydrochloride in 7.5 ml. of hydrochloric acid (sp. gr. 1.19) and 7.5 ml. of water was cooled to 0° C. with stirring. About 0.5 g. of zinc chloride was added to this solution and it was filtered. The filtrate was treated with 1 ml. of 5 M sodium nitrite solution and allowed to stand in the cold for one-half hour. The yellow precipitate was filtered and dried. It probably had the structure:

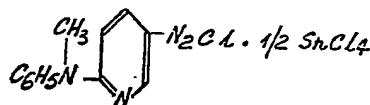
5,5¹ - Diamino - 2,2¹ - (*p,p*¹ - methylenedianilino)dipyridine hydrochloride was prepared by the reduction of 3.4 g. of 5,5¹ dinitro-2,2¹-(*p,p*¹ - methylenedianiline)dipyridine in 200 ml. of ethanol and 50 ml. of acetone under 3—4 atmospheres pressure of hydrogen over palladium on carbon catalyst. The catalyst was filtered off and the filtrate was treated with a few drops of hydrochloric acid (sp. gr. 1.19). 1.7 g. of a solid which darkened at 200° C. and melted at 235° C. with decomposition was isolated.

5,5¹ - Dinitro - 2,2¹ - (*p,p*¹ - methylenedianilino)dipyridine, m. 203—7° C., was obtained by the condensation of *p,p*¹-methylenedianiline with 2 - chloro - 5 - nitropyridine (Example II).

EXAMPLE XII.

N-Methyl-6-anilino-3-pyridinediazonium chloride.

A solution of 2.3 g. of N-methyl-2-anilino-5 - nitropyridine in 200 ml. of isopropyl alcohol was reduced under 3—4 atmospheres pressure of hydrogen over palladium on carbon catalyst. The catalyst was filtered off and the filtrate was treated with a few drops of hydrochloric acid (sp. gr. 1.19) and then drowned in an excess of ether. The white precipitate was very hygroscopic and could not be easily handled in air. It was, therefore, dissolved in 5 ml. of hydrochloric acid (sp. gr. 1.19) and 5 ml. of water, cooled to 0° C. with stirring, and treated slowly with 2 ml. of 5 M sodium nitrite solution. The addition of a few ml. of concentrated stannic chloride solution precipitated a yellow solid which after trituration with ether was filtered and dried. It weighed 3.0 g., melted with decomposition over the range 145—7° C., and probably had the structure:



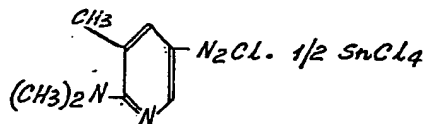
N - methyl - 2 - anilino - 5 - nitropyridine, m. 102—4° C., was prepared by condensation of N - methylaniline with 2 - chloro - 5 - nitropyridine (Example II).

EXAMPLE XIII.

6-Dimethylamino-5-methyl-3-pyridinediazonium chloride.

A solution of 3.0 g. of 5-amino-2-dimethylamino - 3 - methylpyridine hydrochloride in 2.5 ml. of hydrochloric acid (sp. gr. 1.19) and 2.5 ml. of water was cooled with stirring to 0° C. and treated with 3.2 ml. of 5 M sodium nitrite below 5° C. About 2 ml. of a concentrated stannic chloride solution were added and the mixture was stirred for about one-half hour. The yellow precipitate was filtered, washed with a little water, and dried. It weighed 4.0 g., melted with decomposition over the range 135—7° C., and probably had the structure:

position over the range 135—7° C., and probably had the structure:



5 - Amino - 2 - dimethylamino - 3 - methylpyridine hydrochloride was prepared by reduction of 17.3 g. of 2 - dimethylamino - 3 - methyl - 5 - nitropyridine in 250 ml. of ethanol under 3—4 atmospheres of hydrogen-pressure over palladium on carbon catalyst. The catalyst was filtered off and the filtrate was treated with a few drops of hydrochloric acid (sp. gr. 1.19) and then was poured into about 10 times the volume of ether. The white precipitate was collected by filtration and recrystallized from ethanol. It weighed 3.0 g. and melted over the range 221—4° C. with decomposition.

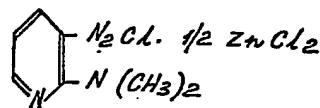
2 - Dimethylamino - 3 - methyl - 5 - nitropyridine, m. 181—91° C., was prepared by the condensation of dimethylamine with 2-chloro - 3 - methyl - 5 - nitropyridine in 96% yield.

2 - Chloro - 3 - methyl - 5 - nitropyridine, b. 144—9°/19mm., was prepared from 2-amino - 3 - methylpyridine in 46% yield J. Org. Chem. 14, 328—32 (1949)).

EXAMPLE XIV.

2-Dimethylamino-3-pyridinediazonium chloride.

A solution of 6 g. of 3 - amino - 2 - dimethylaminopyridine hydrochloride in 15 ml. of hydrochloric acid (sp. gr. 1.19) and 15 ml. of water was cooled to 0° C. with stirring. A solution of 8.6 ml. of 5 M sodium nitrite was added slowly to the solution which took on a deep red color. Five ml. of 70% zinc chloride solution were added and the orange-colored product was filtered, washed with a little water, and dried. It weighed 2.1 g., melted at 185—90° C. with decomposition, and probably had the structure:



3 - Amino - 2 - dimethylaminopyridine hydrochloride, b. 111° C./12mm., was prepared from 3 - amino - 2 - chloropyridine as outlined by Rudy and Majir (Ber. 71B, 1328 (1938)).

3 - Amino - 2 - chloropyridine, m. 75.5—77° C., was prepared from 3 - aminopyridine according to Ber. 69B, 2593—2605 (1936).

Certain of the compounds produced in accordance with the above examples were

tested by incorporating them together with couplers in a sensitizing solution, coating the solution on a base, exposing the coating to actinic light under a positive original and then developing the exposed coating. These tests are described in the following examples: 5

EXAMPLE XV

A solution was made up of the following composition:

Acetone	35 ml.
Methanol	55 ml.
2-Methoxyethyl acetate	10 ml.
Sulfosalicylic acid	1.0 g.
Thiourea	0.5 g.
Zinc chloride	0.4 g.
N-o-methoxyphenyl-3-hydroxy-2-naphthamide	2.0 g.
6-Dimethylamino-3-pyridinediazonium chloride:stannic chloride (Ex. I)	1.6 g.

- 10 This solution was bead-coated on cellulose acetate base. This diazotype material was then exposed under a positive original to actinic light and developed with moist ammonia vapors. A positive diazotype image of purple hue and with a clean white background resulted.
- 15 A solution prepared by substituting 2.0 g. of *m*-hydroxyphenylurea for the N-o-methoxyphenyl-3-hydroxy-2-naphthamide and reducing the amount of 6-dimethylamino-3-pyridinediazonium chloride:stannic chloride from 1.6 g. to 1.0 g. was similarly coated on cellulose acetate to give a positive-working diazotype material. In this case, the image hue was a rich orange-sepia. 20

EXAMPLE XVI

The following solution was coated on cellulose acetate base:

Acetone	35 ml.
Methanol	55 ml.
2-Methoxyethyl acetate	10 ml.
Sulfosalicylic acid	1.0 g.
Thiourea	0.5 g.
Zinc chloride	0.4 g.
<i>m</i> -Hydroxyphenylurea	2.0 g.
6-Anilino-3-pyridinediazonium chloride:zinc chloride (Ex. IX)	1.6 g.

- The intensely yellow colored product was exposed to actinic light under a positive original. The yellow color bleached where light struck, and the positive image was developed with moist ammonia vapors. The resultant diazotype was orange-yellow on a white background and had good reprint opacity to actinic light. 30

A diazotype of essentially the same characteristics was prepared by substituting 6 - p-toluidino - 3 - pyridinediazonium chloride: zinc chloride in the above formulation. 5

EXAMPLE XVII

A solution of the following composition was coated on cellulose acetate film base:

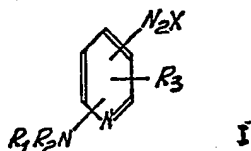
Acetone	35 ml.
Methanol	55 ml.
2-Methoxyethyl acetate	10 ml.
Sulfosalicylic acid	1.0 g.
Thiourea	1.0 g.
Zinc chloride	0.5 g.
<i>m</i> -Hydroxyphenylurea	2.0 g.
6-Dimethylamino-5-methyl-3-pyridine-diazonium chloride:stannic chloride (Ex. XIII)	1.2 g.

The sensitized diazotype material thus produced, pale yellow in color, was exposed to actinic light under a positive original. Treatment with ammonia vapors produced a positive yellow dye image.

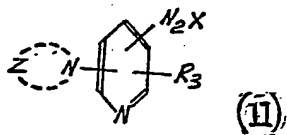
Modifications may be resorted to within the scope of the appended claims.

15 WHAT WE CLAIM IS:

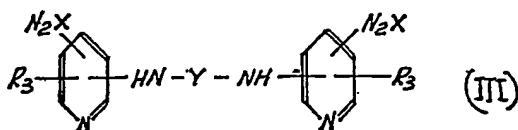
1. An aminopyridinediazonium salt having the general formula:



or the general formula



or the general formula



wherein R₁ is hydrogen, alkyl, aryl of the benzene series, pyridyl or aralkyl; R₂ is alkyl, aryl of the benzene series, pyridyl or aralkyl; R₃ is hydrogen or alkyl; Z represents the atoms necessary to complete a hydrogenated 6-membered heterocyclic nucleus; Y is diphenyl or benzylphenyl; and X is an anion. 25

2. 6 - Dimethylamino - 3 - pyridinediazonium chloride. 30

3. 6 - Methylamino - 3 - pyridinediazonium chloride.

4. 6 - Morpholino - 3 - pyridinediazonium chloride. 35

5. 6 - Piperazino - 3 - pyridinediazonium chloride.

6. 6 - Benzylamino - 3 - pyridinediazonium chloride.

7. 6 - *p* - Toluidino - 3 - pyridinediazonium chloride. 40

8. 6 - (*p* - Dimethylaminoanilino) - 3 - pyridinediazonium chloride.

9. N,N¹ - (4,4¹ - Biphenylene)bis(6 - amino - 3 - pyridinediazonium chloride). 45

10. 6 - Aniline - 3 - pyridinediazonium chloride.

11. 6 - (2 - Pyridylamino)3 - pyridinediazonium chloride.

12. 6,6¹ - (*p,p*¹ - Methylene dianilino)bis(3 - pyridinediazonium chloride). 50

13. N - methyl - 6 - anilino - 3 - pyridinediazonium chloride.

14. 6 - Dimethylamino - 5 - methyl - 3 - pyridinediazonium chloride. 55

15. 2 - Dimethylamino - 3 - pyridinediazonium chloride.

16. Light - sensitive diazotype material.

containing a diazonium salt claimed in any
of Claims 1 to 15.

17. A method of preparing the compound
claimed in claim 1 substantially as herein de-
5 scribed and exemplified.

18. The compound produced by the method
claimed in claim 17.

MEWBURN, ELLIS & CO.,
70 & 72, Chancery Lane, London, W.C.2,
Chartered Patent Agents.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1961.
Published by The Patent Office, 25, Southampton Buildings, London, W.C.2, from which
copies may be obtained.

1872.